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Observation of fluorine-vacancy complexes in silicon

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We show direct evidence, obtained by positron annihilation spectroscopy, for the complexing of fluorine with vacancies in silicon. Both float zone and Czochralski silicon wafers were implanted with 30 keV fluorine ions to a fluence of 2×10^{14} ions/cm², and studied in the as-implanted condition, and after annealing to 650° C for 10 and for 30 minutes. The “2-detector” background reduction technique for positron annihilation was applied. The spectra reveal a significant concentration of fluorine-vacancy complexes after annealing, for both Czochralski and float zone material, supporting the results of computer simulations of the implantation and annealing process.

Fluorine as a dopant in silicon has been an active research area recently, due to a complex set of behaviors including complexing with both vacancies and interstitials. Fluorine in silicon exhibits the ability to retard the diffusion of boron, either when co-implanted as BF₂, or as separate implants, a potential strategy for ultrashallow junction technologies [1-4]. However a more complete understanding of F diffusion behavior, and complexing with defects, is required.

It has previously been reported by Czeles *et al* [5] that open-volume defects introduced by 30 keV F implantation to a fluence of $1 \times 10^{13} \text{ cm}^{-2}$ were completely removed by a 30 minute anneal at 550, 650 or 750 °C. This conclusion was based on positron annihilation measurements with a positron S-parameter near to that for defect-free silicon. Our results are in conflict with these; the 2-detector technique used here provides more detailed information, and allows access to regions of the annihilation spectra which were not accessible to Czeles *et al*.

Recent work by Pi *et al* [6] using positron annihilation suggests that F retards vacancy-interstitial recombination by forming complexes with both interstitials and vacancies. Their results are consistent with the modeling results of Robison *et al* [7], which also yield excellent agreement with Secondary Ion Mass Spectroscopy (SIMS) data for the fluorine profile as a function of post-implantation annealing, across a range of ion fluences and anneal temperatures. The simulations by Robison [7] indicate that after annealing, the remaining defects are interstitial complexes, FI_2 and F_2I_3 , and fluorine-vacancy complexes, FV. In the present work we experimentally verify the presence of FV. Positron annihilation is likely insensitive to interstitial complexes, due to the lack of an “open volume” component in them.

In this paper we report the first direct observation of fluorine-vacancy complexes, using the so-called “2-detector” method of positron annihilation spectroscopy, which uses a coincidence-based method of background reduction to extend the range of the positron spectra, and makes it possible to identify “fingerprints” of elements surrounding the

annihilation site. The application of this method to problems in silicon doping has previously been shown by the observation of vacancy-arsenic complexing in arsenic-doped silicon [8,9]. The method has also been shown to be applicable for a range of other materials, see e.g. [10-12].

Silicon wafers of two types (float zone, *p*-type $\sim 1 \times 10^{14} \text{ cm}^{-3}$, and Czochralski, *n*-type $\sim 1 \times 10^{14} \text{ cm}^{-3}$) were implanted with fluorine to a fluence of $2 \times 10^{14} \text{ ions/cm}^2$ at an energy of 30 keV. The projected ion range is $\sim 70 \text{ nm}$. Three samples of each type were analyzed: as implanted, and after annealing at 650°C for 10 minutes and for 30 minutes.

Simulations using TRIM [13] predict vacancy-interstitial pair production at a rate of ~ 560 per ion for these implant conditions. Allowing that typically 90-95% of these will recombine during and shortly after implantation leaves of order of 50 vacancies and interstitials per F ion, or a concentration of $\sim 10^{21} / \text{cm}^3$. This greatly exceeds the F concentration of $2 \times 10^{19} / \text{cm}^3$, and also the background doping concentration, and the concentration of impurities such as O and C. The interactions among these defects and impurities during post-implant annealing profoundly impacts the electrical properties of the resulting material.

Previously reported [7] SIMS (secondary ion mass spectroscopy) data obtained from similarly prepared samples indicates that for these implant and anneal conditions, annealing sharpens the F profile by increasing the slope on the deeper side of the peak. The profile motion is complete after 30 minutes of annealing. This process has been successfully modeled by computer simulation [7], with the following key features: following implantation, most of the fluorine becomes bound as fluorine-vacancy (FV) complexes. During annealing, these dissociate and immobile fluorine-interstitial complexes, FI_2 and F_2I_3

are formed. Positron annihilation is likely insensitive to these, since they do not have the open volume needed for a positron trap. Simulations show that some FV remain after annealing, and positron annihilation provides experimental confirmation of this aspect of the model.

Positron annihilation spectroscopy was used to probe defects in the material. Positrons are implanted into the samples, to a depth controlled by varying the implantation energy. The positron then diffuses thermally until either (a) it annihilates with an electron, or (b) it is trapped by a defect, such as a vacancy. The annihilation results in two gamma rays in (approximately) opposite directions. These carry off the momentum of the annihilating electron, and so an energy spectrum of the gamma rays, obtained with a large Ge detector, contains information regarding the annihilating electrons. Besides the ability to obtain approximate concentrations of vacancy-type defects, it has become possible to interpret features of the spectra to identify impurities surrounding the annihilation site: the electron energies are elementally-specific, and so each element provides a characteristic “fingerprint” in the spectrum. In practice we are not usually interested in identifying an element from among numerous possibilities, but simply in identifying whether an element known to be present in the sample (in this case F) is attached to the vacancies that trap the positrons. A complication arising in studies of silicon is the ubiquitous presence of O as an impurity.

Figure 1 shows positron annihilation “low momentum fraction”, also called the “S parameter” (a measure of open volume in the sample) for both Cz and FZ silicon implanted with $2 \times 10^{14}/\text{cm}^2$ 30 keV fluorine, before and after annealing. These data are normalized to a

value of 1.00 for the undamaged silicon substrate. Examining the data for the as-implanted samples, we find $S > 1.0$, due to vacancy-type defects in the implanted regions. There is an apparent difference in depth of the damage, Cz versus FZ, however this is likely due to positron diffusion induced by electric fields in the samples, and may not reflect a real difference in depth of the damage [14]. After sample annealing, the positron data yield S-parameter values $S < 1$, indicative of vacancy-impurity complexes. Based on these data alone, it is not possible to state with certainty whether the positron-trapping defect is FV or alternatively a complex involving oxygen: the value of S obtained is consistent with those previously reported for SiO_2 [15]. However the appearance of $S < 1$ for both FZ and Cz wafers, despite very different oxygen concentrations, suggests that FV is present.

It has previously been shown [14] that positron spectra from bulk-doped silicon are identical regardless of dopant species and concentration, provided that the dopant is not attached to a positron-trapping defect such as a vacancy.

For more compelling evidence of FV complexes, we apply a refinement of the positron beam technique (described above) and examine the spectra shown in figure 2. These spectra of momentum vs relative intensity are obtained using the 2-detector coincidence technique, and are normalized to spectra for undefected silicon, as a means to emphasize the differences among spectra [details of this technique are discussed in refs. 12 and 16]. The spectra obtained from annealed samples show a clear F “fingerprint”. Again we need to eliminate the possibility that what we are observing is due to oxygen, which exhibits a similar (but not identical) annihilation “fingerprint” [12]. To do this, we attempted to match the sample spectra using combinations of spectra from Si, SiO_2 , and

NaF. (We have obtained nearly identical spectra for NaF, LiF, and MgF_2 , and we assume these are representative of the negative anion F). We found that the combination $0.622 \text{ NaF} + 0.387 \text{ Si}$ yields an excellent fit to data from the 30-minute annealed FZ sample (see figure 3). We also found that $\text{Si} + \text{SiO}_2$ in any proportion does not match the data. The FZ sample annealed for 10 minutes was well matched by $0.544 \text{ NaF} + 0.456 \text{ Si}$. The Cz samples yielded similar results despite their greater O concentration, and thus we conclude that we are observing FV complexes in the annealed samples.

It is difficult to make quantitative interpretation of these peak heights (i.e. at this time the theoretical calculations are not sufficiently advanced) however we can make some estimates as follows. For the previously-studied case of As in silicon, with an estimated average of ~ 3 As atoms surrounding a silicon vacancy, an As peak height of ~ 1.5 has been reported, representing $\sim 75\%$ of the height obtained for pure As [8]. In our case we have a height of 2.5, or $\sim 64\%$ of the height for NaF of 3.9. Thus we can very crudely assume that a similar average of 2-3 fluorine atoms might surround the annihilation site in our samples.

We have shown direct evidence for FV complexes in silicon following F implantation and annealing. This supports computer modeling results [7]. Computer modeling also predicts the presence of fluorine-interstitial complexes, but these are inaccessible to positron techniques. We also suggest that O does not play a major role in this process, based on the similarity of results obtained for FZ and for Cz silicon.

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Figure Captions

Figure 1: Positron “low momentum fraction”, or S-parameter, for Si implanted with 30 keV F, $2 \times 10^{14} \text{ cm}^{-3}$, and annealed. Values greater than 1.0 indicate open-volume defects. We attribute values less than 1.0 (in these samples only) to FV complexes.

Figure 2: Positron spectra, normalized to the spectrum for silicon, showing relative intensity vs. electron momentum. Peaks in the data from annealed samples match the “fingerprint” of fluorine.

Figure 3: Data for the FZ 30 minute annealed sample can be constructed by summing spectra from NaF and Si, supporting the interpretation that the peak observed is due to fluorine.

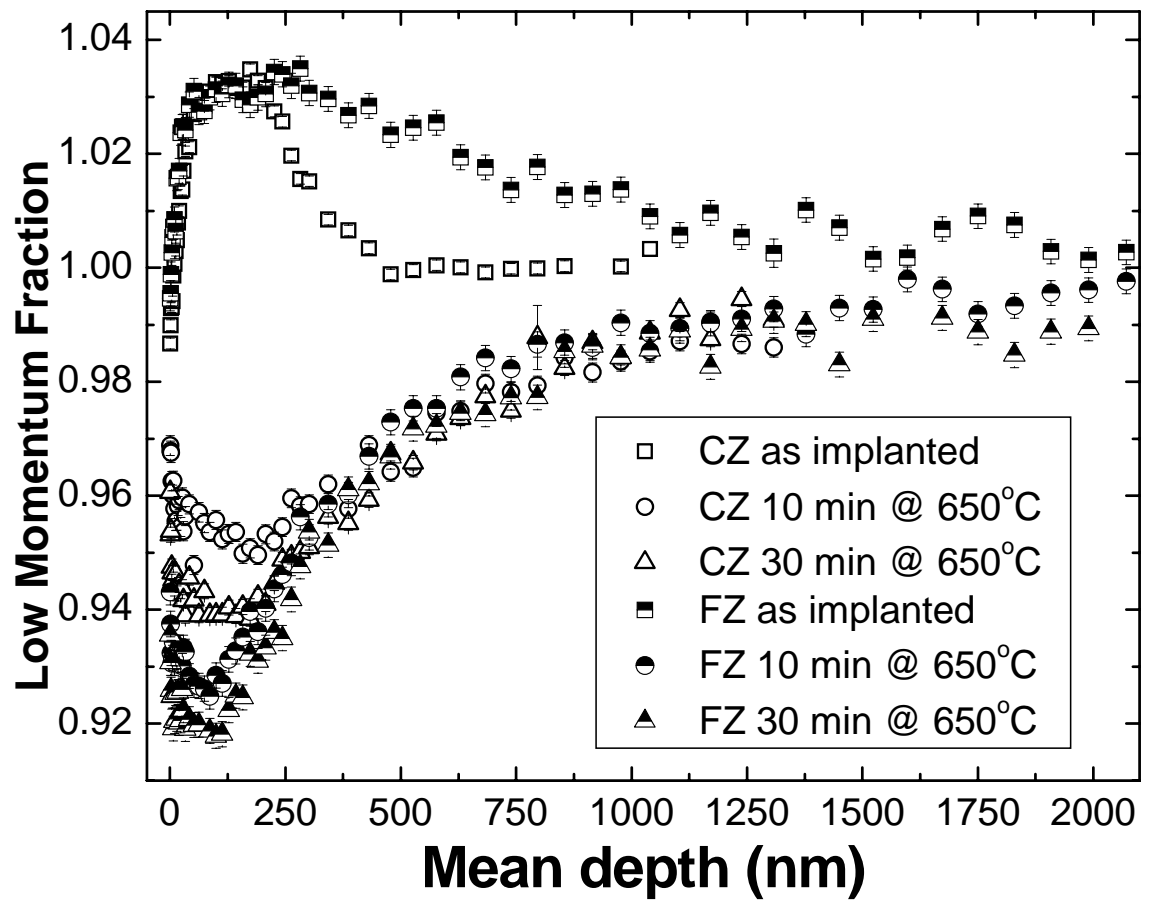


Figure 1

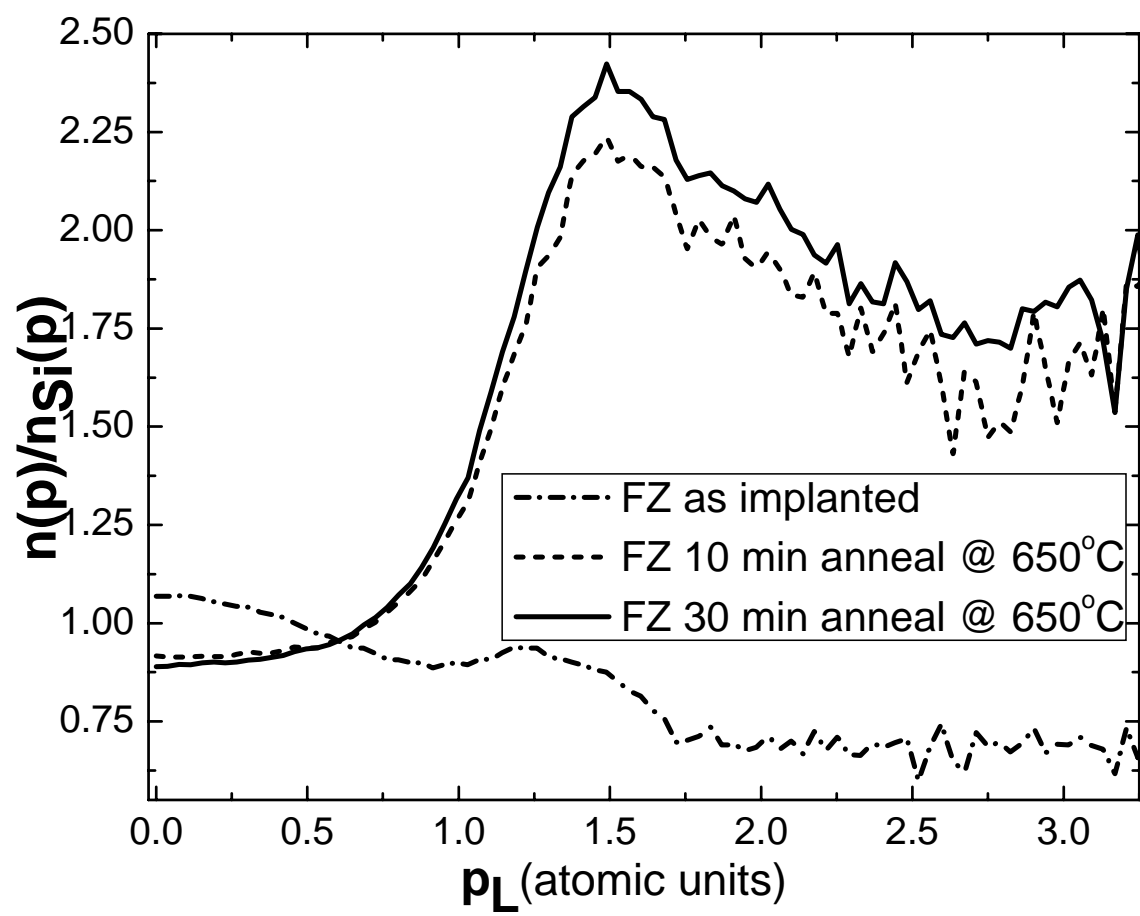


Figure 2

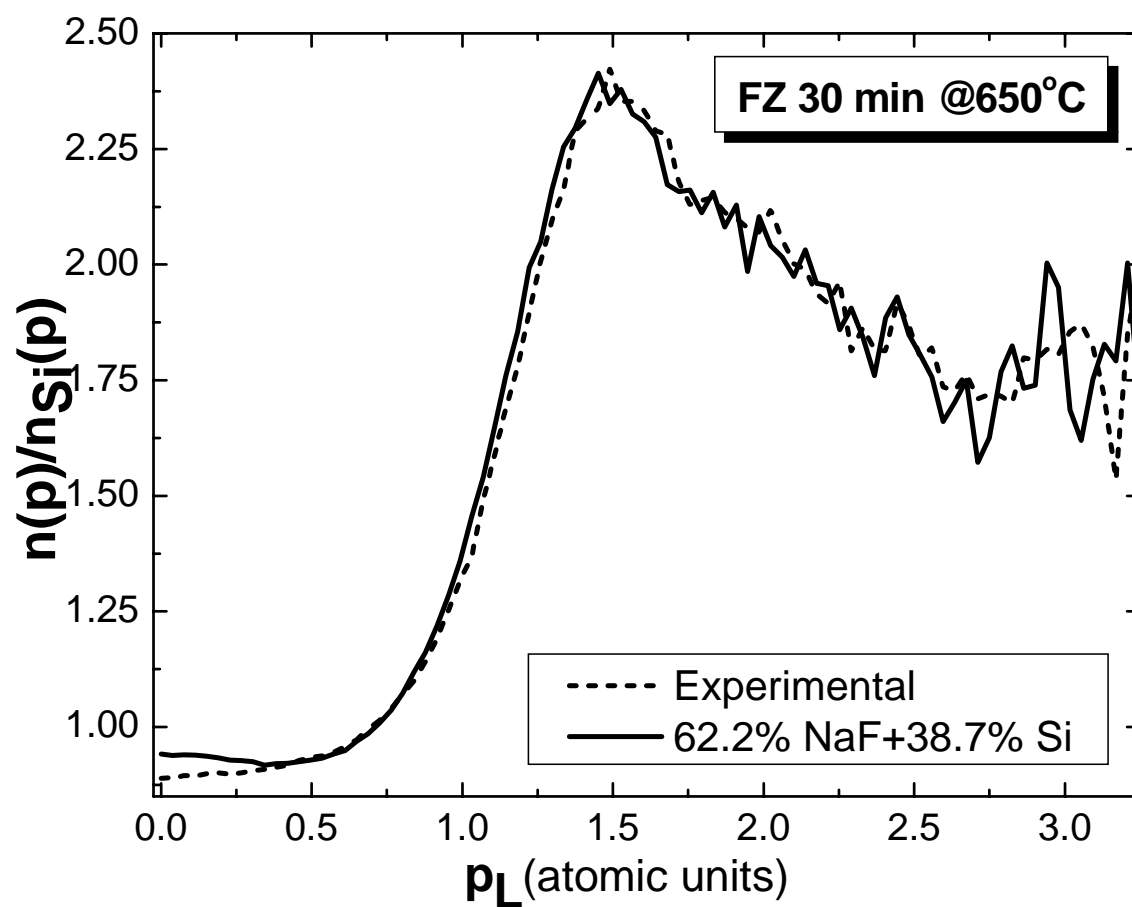


Figure 3